XV.—*On some New Basic Products obtained by the Decomposition of Vegetable Alkaloids.*

By Henry How, Esq., F.C.S.

ASSISTANT TO PROFESSOR ANDERSON, OF GLASGOW.

In the following pages, I purpose submitting to the notice of the Society the results of some experiments, so far as I have proceeded with them, on the action of the halogen-compounds of the alcohol radicals on bases of vegetable origin. The beautiful researches of Hofmann on the behaviour of artificial liquid bases and of ammonia, under these circumstances, led him to remark that a similar course of investigation, in regard to basic substances generally, would no doubt tend to throw much light on the nature of these bodies. On comparing the formulæ of some of the vegetable alkaloids with which I was best acquainted, their relations to each other were such that I was curious to bring to light the result of experimenting upon some of these substances in the direction mentioned.

The established formula for morphia, which was first given as the correct interpretation of the analysis of the pure alkaloid by Laurent,* and which I have confirmed by experiments of my own, is

$$C_{34}H_{19}NO_6.$$

It will be seen, by a comparison of this formula with that of codeine, as established beyond a doubt by Professor Anderson,†

$$C_{36}H_{21}NO_6,$$

that these alkaloids differ from each other exactly by C_2H_2. Now, reasoning from analogy, if these bases follow the same laws of decomposition as their volatile congeners, I should, by the action of iodide (*e. g.*) of methyl upon morphia, obtain either codeine or a base having the same centesimal composition, according to the reaction expressed in the equation:

$$C_{34}H_{19}NO_6 + C_2H_3I = C_{36}H_{21}NO_6 = C_{34}\left\{\begin{matrix}H_{19}\\C_2H_2\end{matrix}\right\}NO_6 + HI.$$

It was with this idea that I commenced the following series of experiments; and although the reaction represented above was not that which I studied first—for iodide of ethyl was ready to my hand—the results which I obtained with this compound, though not such as to render me sanguine as to the actual conversion of the one

* Ann. Ch. Phys. [3], XIX. † Trans. Roy. Soc. Edinb. XX, I, 57.

alkaloid into the other—a problem which has engaged the attention of chemists of great name*—were sufficiently marked in character to urge me to prosecute the inquiry, with what success will be seen in the sequel.

If, in the succeeding pages, the numbers given in one or two instances fall somewhat below the standard of accurate analytical proof, I trust that, to those acquainted with the nature of the materials employed, the mention of their costly character will be sufficient excuse for a want of repetition of experiments where a great deal would not have been gained by the same; believing that sufficient evidence is furnished as to the composition at least of the substances produced. I beg here to offer my most sincere thanks to Professor Anderson, in whose laboratory, attached to the University of Glasgow, my experiments were performed, for the opportunity of conducting this inquiry.

In detailing the investigation, I have preferred to narrate the individual reactions, &c., in the order in which they were examined.

ACTION OF IODIDE OF ETHYL UPON MORPHIA.

Morphia, in a state of fine powder, was introduced into a combustion-tube, strongly sealed at one end, a little iodide of ethyl added, and then absolute alcohol, in quantity judged to be sufficient to dissolve the alkaloid. I found about 25 grains might be conveniently employed in a tube of small bulk; and alcohol occupying about three times the space of the alkaloid was found sufficient, a very small quantity of iodide of ethyl being required. When the substances were all introduced, the tube was carefully sealed before the blow-pipe, and upon its cooling, the whole was immersed in boiling water. Complete solution took place when a small quantity of morphia was employed, but not so when more was used; action commenced very speedily, as was obvious from the nature of the solid product in the tube, which had not the appearance of morphia. The boiling was continued some hours when complete solution had not taken place at first, in order that any morphia which had at first remained undissolved might in its turn be acted upon, as the alcohol became free, as it were, by deposition of the new product. When the action had continued about six hours or so, the tube was allowed to cool, and then opened; the alcohol containing the excess of iodide of ethyl, nearly colourless and quite limpid, was poured off from the white crystalline solid product, which was then washed with a little

* Ann. Ch. Pharm. XXVI, 60.

alcohol, and dried. It was found to dissolve readily in hot water; accordingly, the whole was treated in this manner, in case of any morphia remaining unattacked, from which, it being insoluble or very difficultly soluble in this menstruum, the product would by this means be purified. However, complete solution took place; and the fluid deposited, on cooling, a substance in fine white needles; these were collected, dried and analyzed, a preliminary experiment having shown that they contained much iodine.

In the following analysis, the iodine was determined by direct precipitation of an aqueous solution by nitrate of silver; the combustion made with chromate of lead:

5·155 grs., dried at 212°, gave
9·725 „ carbonic acid, and
2·665 „ water.
4·470 „ gave
2·365 „ iodide of silver.

	Experiment.	Calculated.		
Carbon	51·45	51·71	C_{38}	228
Hydrogen	5·74	5·44	H_{24}	24
Nitrogen		3·17	N	14
Oxygen		10·87	O_6	48
Iodine	28·59	28·81	I	127·1
		100·00		441·1

A comparison of the experimental numbers with the calculation appended, will show that we have here a substance which may be termed the hydriodate of ethylomorphia, and whose constitution may be represented by the formula,

$$C_{34}\left\{\begin{matrix}H_{18}\\C_4H_5\end{matrix}\right\}NO_6,\ HI,$$

an atom of hydrogen of the original alkaloid being replaced by an atom of ethyl in the production of the new base, according to the equation,

$$C_{34}H_{19}NO_6 + C_4H_5I = C_{38}H_{23}NO_6,\ HI = C_{34}\left\{\begin{matrix}H_{18}\\C_4H_5\end{matrix}\right\}NO_6,\ HI.$$

The above salt is the only product of this decomposition, and the entire morphia is transformed into it: in the air-dry state, as crystallized from water, it contains an equivalent of water, which it loses at 212°.

{ 9·805 grs. air-dry, lost in the water-bath
{ 0·195 „ water.

The percentage calculated from this result is 1·98, and 1·98 is that corresponding with the formula :

$$C_{38}H_{23}NO_6, HI + aq.$$

Hydriodate of ethylomorphia is difficultly soluble in absolute alcohol, more easily so in rectified spirit: readily dissolved by hot water, from which it is deposited on cooling in brilliant colourless crystals, which magnifying power shows to be flattened prisms : it is not altered in the air.

Neither potash nor ammonia yielded a precipitate with an aqueous solution of this salt ; but, before attempting to isolate the base which this fact pointed out would have to be sought in another way, I attempted to control the above formula by an analysis of a platinum-salt,but was unsuccessful. A saturated aqueous solution of hydriodate of ethylomorphia was converted into hydrochlorate by the successive employment of nitrate of silver and hydrochloric acid, and to the clear aqueous solution so obtained, bichloride of platinum was added; no precipitate was formed : a mixture of strong alcohol and ether was added to a small quantity of this solution, and it and the remaining aqueous fluid were allowed to stand during a night ; in the morning the former fluid had deposited beautiful tufts of brilliant yellow needles which, though small, were seen when magnified to be well-defined groups of prismatic crystals, while at the bottom of the larger aqueous liquid was an amorphous yellow sediment; this was collected and burned in the usual way, but the resulting percentage of platinum was 2·5 too high to correspond with the theory. I look upon this as an effect of decomposition; and in this respect the new base seems to bear a close analogy with its parent alkaloid, which I have found very prone to change in contact with an excess of bichloride of platinum.

In order to obtain the base, a quantity of the crystallized hydriodate was dissolved in water gently heated, and oxide of silver gradually added till it was in excess. The fluid remained colourless so long as hydriodate was present, but instantly a decided excess of oxide of silver prevailed, dark streaks appeared, and upon filtration a highly caustic liquid was obtained, of a red-brown colour ; this deposited no crystals upon cooling, or upon concentration, and when the whole was evaporated to complete dryness at 212°, a semi-transparent, solid, very dark-coloured residue was obtained.

This residue was found to be difficultly soluble in strong alcohol

(90 per cent), and a boiling solution deposited a substance amorphous to the naked eye, but revealing under the microscope distinct crystalline structure; it was scarcely altered in appearance by exposure to the air; but upon adding hydrochloric acid to a portion so exposed, it was observed to dissolve with slight but distinct effervescence to a yellow fluid, which gave a heavy yellow precipitate with chloride of platinum. It was readily and completely soluble in cold water to a red-brown fluid, which exhibited the following behaviour with various re-agents: with bichromate of potash a fine heavy yellow precipitate, soluble in hydrochloric acid; the acid solution became speedily green upon heating from reduction of the chromic acid;—with sulphate of copper a green, with acetate of lead a white, and in excess with nitrate of silver a black precipitate. The latter precipitate, upon the fluid in which it had been formed being heated, gave a slight metallic mirror, and was found to be not completely soluble in ammonia, showing that the base had been oxidized at the expense of the oxide of silver. When it was added to an aqueous solution of sesquichloride of iron, the latter assumed a green colour, darkening to an almost black fluid, with a larger quantity of the alkaline solution, and it was then found to give a blue precipitate with ferridcyanide of potassium, from which fact it is plain, that in this instance also the base had undergone oxidation: ammonia was evolved on heating solution of chloride of ammonium with the alkaline fluid.

Consideration of the foregoing reactions did not permit me to hope for a succcessful analysis of the alkaline residue, as the pure ethylomorphia; however I made the attempt:

$$\left\{\begin{array}{l} 4{\cdot}040 \text{ grs. dried at } 212^0, \text{ gave} \\ 10{\cdot}130 \text{ ,, carbonic acid, and} \\ 2{\cdot}505 \text{ ,, water.} \end{array}\right.$$

The percentages calculated from these numbers, I place in juxtaposition with the required values for the base:

	Experiment.	Calculated for ethylomorphia.		
Carbon . .	68·38	72·84	C_{38}	228
Hydrogen .	6·88	7·34	H_{23}	23
Nitrogen .		4·47	N	14
Oxygen .		15·35	O_6	48
		100·00		313

and the conclusion I draw from the comparison is, that the ethylomorphia I subjected to analysis had already undergone partial oxi-

dation from contact with oxide of silver. I cannot at present add anything to this imperfect history, for my material was exhausted in the experiments described, but sufficient is shown, I think, to make future inquiry of interest. It is obvious the base is extremely prone to decomposition by oxidizing agents; in this character it also resembles its parent morphia, but it shows the tendency in a more marked degree.

I did not attempt to continue the ethylation in this case, a trial of the kind being made with the methyl-product to be next described.

ACTION OF IODIDE OF METHYL UPON MORPHIA.

Morphia was submitted to the action of iodide of methyl under precisely the same circumstances as have been described with reference to iodide of ethyl; after about half an hour's boiling, the change appeared complete, a heavy white crystalline powder, occupying a larger space than the original alkaloid, being formed. The fluid remained almost colourless, and drained away readily from the new product when the tube was opened.

The product was found to dissolve readily in hot water, showing that complete change had taken place. As the water cooled, a deposit was quickly formed in fine brilliant, square, prismatic, colourless needles, of high refractive power. A portion was analyzed in the same manner as the former product:

4·455 grs. dried at 212° gave
8·245 „ carbonic acid, and
2·152 „ water.
4·335 „ give
2·380 „ iodide of silver.

	Experiment.	Calculated.		
Carbon . .	50·47	50·57	C_{36}	216
Hydrogen .	5·36	5·15	H_{22}	22
Nitrogen .		3·27	N	14
Oxygen .		11·26	O_6	48
Iodine . .	29·66	29·75	I	127·1
		100·00		427·1

These results point to a decomposition precisely analogous, as was to be anticipated, to the one with iodide of ethyl; the hydriodate of methylomorphia being formed according to the equation

$$C_{34}H_{19}NO_6 + C_2H_3I = C_{36}H_{21}NO_6HI = C_{34}\left\{\begin{matrix}H_{18}\\C_2H_3\end{matrix}\right\}NO_6HI.$$

The salt in the crystallized state contans 2 equivs. of water which it loses at 212°.

9·630 grs. lost on drying in the water-bath
0·400 „ water.

The percentage calculated from this number is 4·15; and 4·04 is that which corresponds to the formula

$$C_{36}H_{21}NO_6 + 2\,HO.$$

This is precisely the formula found for the hydriodate of codeine as dried at 212°, by Professor Anderson;* so that the air-dry hydriodate of methylomorphia is identical in composition with the corresponding salt of codeine as dried at 212°; the salts, however, are only isomeric, for nothing could be more unlike the fine crystalline alkaloid codeine, than the alkaline substance obtained by the action of oxide of silver upon the hydriodate of the new base. In short, it resembles in every particular the corresponding ethyl-compound in appearance and reactions so closely, that to describe them would be to repeat what has been said of that substance. I did not attempt an analysis of this base, but having obtained some in the dry state, proceeded to try the further action of iodide of methyl upon it.

With this view, the base was separated by the action of oxide of silver, of which an excess was attempted to be avoided, on the hydriodate, and subsequent evaporation of the caustic aqueous fluid, which was coloured reddish-yellow, to dryness at 212°; in this state it presented an appearance as beforesaid, exactly similar to that of ethylomorphia, produced by the same means, namely, that of a dark-brown, semi-transparent, amorphous mass. Its reactions were identically those of the former base. The methylomorphia so obtained had most probably commenced to undergo partial oxidation, but as this was unavoidable, the whole was powdered and placed in contact with iodide of methyl and alcohol. Action commenced even in the cold; for on shaking together the contents of the vessel, the fluid became filled with a light-brown flocky substance, which upon trial gave a precipitate with nitrate of silver, showing the presence of hydriodic acid. To ensure reaction, the tube containing the mixture was sealed, and subsequently placed in water at 212°; upon this a resinous substance was immediately formed at the bottom of the tube, and the supernatant liquid became quite clear, the flocky matter disappearing. The heating was continued about half an hour, and no further change taking place in appearance, the tube was allowed

* Trans. Roy. Soc. Edinb. XX.

to cool; a very slight deposit appeared adhering to the sides of the tube, of rather a resinous nature. The tube was opened, and the clear fluid poured from the resin; water was added to it, no change produced; the aqueous fluid was then distilled, to separate the excess of iodide of methyl, and subsequently evaporated at 212°; the residue left was a black amorphous mass, which was found to dissolve only partially in water to a very dark fluid, while a considerable portion remained in the form of a black powder; this proved to be insoluble in every menstruum, with the exception of strong nitric acid, which gave a reddish-yellow solution, nitrous acid being evolved. The watery fluid contained a hydriodate of a base; the quantity being very small, I attempted to obtain some idea of the change effected by converting it into a platinum-salt, carefully avoiding an excess of platinum-solution. I obtained a yellow curdy salt, but in very small quantity, and on determining the percentage of platinum with the utmost care I obtained 21·14 per cent, which is far above that required by the platinum salt of even morphia itself.

The resinous deposit which was described as adhering to the sides of the tube, appears to be identical with the substance contained in the alcoholic fluid; at least it furnished a solution in hot water, which upon evaporation at 212°, left a residue agreeing in its characters and qualitative reactions precisely with that left by drying up the spirituous liquid; its quantity was too small to admit of quantitative experiments.

I do not venture to draw any definite conclusions from these facts with regard to the continued action of iodide of methyl upon methylomorphia, but that a decomposition of a more complicated nature than the simple assumption of another equivalent of ethyl takes place is, I think, obvious. It will be shown presently that this conclusion seems to be warranted by a deportment of a similar nature observed in reference to a basic product derived from codeine. Further experiment, however, must decide the nature of these changes.

REACTION BETWEEN MORPHIA AND CHLORIDE OF AMYL.

Morphia was placed in contact with chloride of amyl under circumstances precisely similar to those which have been mentioned with regard to iodide of ethyl and methyl. No change took place after three days; for upon opening the tube, the alkaloid was found unaltered. Knowing the reactions of this member of the alcohol series to be somewhat sluggish, I repeated the experiment, expecting a longer exposure to heat might be requisite to effect a decomposition.

Accordingly, a tube was sealed as before, and the contents were kept boiling constantly for about fourteen days. In about four or five days, a crystalline substance began to be formed, and upon opening the tube at the fortnight's end, the solid deposit which had gradually collected, was found to be a hydrochlorate; the alcoholic fluid was poured away and the salt washed and dried; it was soluble in hot water, and the colourless solution gave, upon gentle evaporation, a crystalline substance, in the form of opaque tufts of four-sided prisms (magnified); when dried and subjected to analysis, the crystals gave these results:

I. { 3·060 grs. dried at 212°, gave
   { 1·340 „ chloride of silver.

II. { 4·290 „ dried at 212°, gave
    { 1·895 „ chloride of silver.

	Experiment.		Calculated.		
Carbon . .			63·45	C_{34}	204
Hydrogen .			6·22	H_{20}	20
Nitrogen . .			4·35	N	14
Oxygen . .			14·94	O_6	48
Chlorine . .	10·83	10·92	11·04	Cl	35·5
			100·00		321·5

which, upon a comparison with the calculation, and the formula adjoined, which is that of morphia, will show that we have not in this case a decomposition analogous with the preceding ones; the hydrochlorate here formed is indeed the salt of morphia; its appearance and characters are identical with the latter; and the addition of ammonia to its aqueous solution, yields a crystalline precipitate, which has all the properties of pure morphia, as ascertained by various tests.

The reaction thus occurring may be explained as taking place between the chloride of amyl and the elements of water, of which morphia, as crystallized from alcohol (the state in which it was employed) retains 2 equivs. when dried in the air; indeed, they are not completely expelled, except at a temperature considerably above 212° F. So far as I remember, I used absolute alcohol; and the chloride of amyl had been, I was told, distilled from lime: at all events, when tested with nitrate of silver, it gave only slight indications of chlorine in a state precipitable by this reagent; the equation representing this change then appears to be:

$$C_{34}H_{19}NO_6, 2\,HO + C_{10}H_{11}Cl = C_{34}H_{19}NO_6, HCl + C_{10}H_{12}O_2.$$

I am not aware if the chloride of amyl has been found to undergo this transformation simply in presence of water; possibly it may, under the circumstances of my experiment; if not, the action of the morphia in this respect seems to be analogous to that of potassa, &c., in producing the alcohols from their corresponding halogen compounds.

I propose subjecting artificially dried morphia to the action of anhydrous chloride of amyl, to ascertain if the compound of this series, corresponding to the ethyl and methyl products, cannot be so obtained.

I now proceed to give the result of some experiments upon a vegetable alkaloid, closely allied in origin with the former, viz.: codeine.

ACTION OF IODIDE OF ETHYL UPON CODEINE.

About 25 grains of finely-powdered codeine were placed in a combustion-tube, about 2 feet long, sealed at one end; iodide of ethyl was poured upon it in small quantity, and absolute alcohol added in such proportion as was judged sufficient to dissolve the alkaloid; the tube was sealed. On cooling of the tube, its contents were shaken together, and a perfectly clear homogeneous fluid was obtained: the whole was placed in boiling water. In about two hours, the contents of the vessel became nearly solid, from the presence of a white, crystalline substance. This was considered to indicate the completion of the action.

Upon the appearance of the crystalline product, the tube was allowed to cool. When it was cut open, the fluid was suffered to drain off from the solid, which was then scraped out, placed upon a filter, washed with a little alcohol, and finally dried between folds of paper. The substance then presented the appearance of a highly crystalline, white mass; it was found to dissolve completely, on being covered with a small quantity of cold water. On filtering the fluid from a little dust, a tendency to crystallization was observed: this was overcome by the addition of some drops of warm water, and the clear liquid was placed in the vacuum of an air-pump, and left for a night. In the morning, although the apparent decrease in the bulk of liquid was but small, a considerable crystalline deposit was formed, which, under magnifying power, was seen to be made up of tufts of fine, silky, white needles; it was freed from the mother-liquor, and then collected and dried. An experiment on the small scale showed that the substance contained much iodine; accordingly

it was submitted to analysis. The iodine in the following analysis was determined by direct precipitation of an aqueous solution by nitrate of silver; the combustion made, of course, with chromate of lead:

5·025 grs. dried at 212°, gave
9·690 „ carbonic acid, and
2·658 „ water.
4·453 „ gave
2·300 „ iodide of silver.

Experiment.		Calculated.		
Carbon . .	52·59	52·73	C_{40}	240
Hydrogen .	5·87	5·71	H_{26}	26
Nitrogen .		3·07	N	14
Oxygen .		10·57	O_6	48
Iodine . .	27·91	27·92	J	127·1
		100·00		455·1

These results clearly show that we have here a substance whose rational formula, as an hydriodate of a new base, may be represented thus:

$$C_{40}H_{25}NO_6, HI,$$

derived from codeine, according to the following equation, by the substitution of an atom of ethyl for an atom of hydrogen; it may be called hydriodate of ethylocodeine:

$$C_{36}H_{21}NO_6 + C_4H_5I = C_{40}H_{25}NO_6, HI = C_{36}\left\{\begin{matrix} H_{20} \\ C_4H_5 \end{matrix}\right\}NO_6, HI.$$

I immediately attempted to obtain the base by decomposition of the salt by ammonia and potash, but no precipitate was obtained even in very concentrated solutions, or on the addition of alcohol and ether. However, when the potass-fluid was boiled, it became muddy, and on cooling, an oily substance was deposited, which presented an appearance somewhat similar to codeine; but upon dissolving it in boiling water, it failed to take the crystalline character of this alkaloid under similar circumstances, for the water gave no deposit at all on cooling, and it was only by evaporation that the same oily matter again made its appearance. I am inclined to think this not the ethylocodeine, but a product of decomposition. I next attempted to isolate the base by acting on the hydriodate with oxide of silver, which was added in successive small quantities to a warm aqueous solution of the salt till it was obviously in excess; a highly alkaline

fluid was obtained, of which a small portion was evaporated to dryness at 212°; a semi-transparent, dark-coloured residue remained, which effervesced with hydrochloric acid, and dissolved to a yellow fluid, which gave, with bichloride of platinum, a yellow precipitate, at first amorphous, but becoming highly crystalline on standing; this character, as will be seen presently, belongs to the platinum-salt of ethylocodeine obtained by double decomposition, and I conclude that the new basic substance is uncrystalline, highly soluble in water, and capable of absorbing carbonic acid from the air. The nature of my materials compelled me to extreme economy, and I contented myself with this single attempt at obtaining the base itself in a dry state; its characters not being inviting for analysis any more than those of the corresponding morphia-compound, I preserved the residue of that which I had prepared, for an experiment to be described hereafter, controlling the former analysis of the hydriodate by a platinum determination in the double salt of the ethylocodeine and chloride of platinum.

The mother-liquor which had deposited the hydriodate submitted to analysis, was allowed to stand in the air; it became, after some time, again nearly filled with tufts of delicate needles, which gradually assumed a new crystalline form, the whole being transformed into well-defined, brilliant rhombic crystals of high refractive power. A portion of these was dissolved in water, and solution of nitrate of silver added; from the fluid filtered from the iodide of silver hydrochloric acid separated the excess of silver, and to the liquid again filtered was added bichloride of platinum; an amorphous precipitate immediately appeared of a pale yellow colour, but it speedily became crystalline, and on allowing the fluids to remain at rest, a salt was obtained in very fine, and well-defined, though small, rhombic crystals of a rich yellow colour; of this salt,

$$\left\{\begin{array}{l} 5{\cdot}910 \text{ grs. gave} \\ 1{\cdot}060 \text{ ,, platinum.} \end{array}\right.$$

The percentage calculated from this result is 17·93, which falls somewhat below that required by the formula of an anhydrous salt of ethylocodeine, which is 18·51; but as the salt was so finely crystallized, and I could perceive no obvious source of error, I am inclined to think that this base, like its parent codeine, retains an equivalent of water in this form of combination. The percentage of platinum corresponding to the formula,

$$C_{40}H_{25}NO_6,\ HCl,\ PtCl_2 + HO,$$

is here contrasted with the result of experiment,

Theory.	Experiment.
18·20	17·93

and is, I think, sufficient to prove, together with the foregoing analysis, the true composition of the base in question. When this salt is boiled in water it becomes at first resinous, then dissolves; it appears to have suffered decomposition, a substance being deposited, on cooling of the fluid, in rounded transparent granules, rather than oblique rhombic crystals.

ACTION OF IODIDE OF ETHYL ON ETHYLOCODEINE.

I mentioned that I attempted to isolate ethylocodeine by decomposition of its hydriodate by oxide of silver. A caustic fluid was obtained which, upon evaporation *in vacuo*, left an amorphous semi-transparent residue. I concluded from the experiment then mentioned with regard to a platinum-salt obtained from a similar trial on the small scale, in which the caustic fluid was evaporated to dryness at 212^0, that the base so obtained was the true ethylocodeine.* It was now my object to try, by the further action of iodide of ethyl, whether the ethylation was complete, or if another atom of hydrogen could be taken away and replaced by ethyl. With this view, the residue obtained by evaporation of the alkaline fluid *in vacuo* was dissolved in absolute alcohol, iodide of ethyl added, and the whole sealed up in a tube, which was exposed to the temperature of boiling water; no crystalline deposit appearing, the action was continued for about twenty-four hours; at the end of this time the fluid became rather dark coloured, and a resinous black-looking deposit was formed. The tube was opened, the fluid poured from the deposit into a small flask, and the chief part of the iodide of ethyl distilled off; water was added to the remaining fluid, which was then placed on the water-bath and allowed to remain some hours; at the end of this time all smell of iodide of ethyl ceased, and a black substance deposited in small quantity: the fluid was filtered from this, and upon the addition of nitrate of silver, a considerable precipitate of iodide was formed; the excess of silver was removed by hydrochloric acid, and bichloride of platinum was added to the filtered fluid; an amorphous yellow precipitate was formed which, upon standing, became partially converted into a substance which, under the microscope, appeared not crystalline, but had the form of rounded grains; this was collected and analyzed. The resulting percentage of platinum obtained was 21·20, which is considerably above that of

* Possibly it had undergone slight oxidation.

codeine itself. This, and the appearance of the resinous substance—which I may mention dissolves almost completely in boiling hydrochloric acid, and is again thrown down by potash—seem to point to decomposition of quite another character than the one sought. I am unable at present to elucidate this question, but it seems worthy of investigation. It is perhaps proper to state here, that in the first experiment I made upon the action of iodide of ethyl upon codeine, the action was continued some hours after the first deposit had been observed, and that in this case also a resinous deposit was formed, the fluid was highly coloured, and the crystalline product was not nearly so well-defined in its characters. It was for this reason that the action in the experiment, the product of which gave the results stated, was stopped as soon as the large quantity of crystalline deposit appeared.

I have satisfied myself that codeine is rapidly acted upon by iodide of methyl; no doubt the resulting decomposition is similar in nature to that effected by iodide of ethyl.

The preceding experiments are not complete enough, or in some respects sufficiently decided in their results, to permit of any very definite conclusions being drawn as to the exact nature of the alkaloids to which they relate; so much, however, has been shown, I think, as to call for some attempt at deduction.

The nature of the alkaline substances produced by the action of oxide of silver upon what I have termed the hydriodates of ethylo- and methylo-morphia and codeine, would seem to ally them more closely to what Hofmann has called oxides of tetra-bases than to any other bodies. In the slight but distinct tendency they exhibit to absorb carbonic acid, they are certainly removed from any close analogy with the alkaloids from which they are derived; although, in the single analysis I have given of one of these substances, the so-called ethylo-morphia, the evident oxidation it had undergone prevents any support being afforded to this assumption on the one hand, so likewise on the other it does deprive it of any pretensions to correctness. The only conclusion I can venture to draw from the facts obtained, as to the continued action of the iodides of methyl and ethyl upon these substances, is that some change is effected which causes the formation of a basic body, having a lower atomic weight than the original compound, and the production of the resinous matters seems also to point to a breaking up of the primary molecule; but of course the experiments from which this is inferred are too incomplete to warrant any more decided opinion as to the precise

nature of the decomposition. It would follow necessarily, from the foregoing view of the constitution of the ethyl and methyl new basic compounds isolated from their salts, that if the alkaloids from which they are derived were placed in their appropriate class, according to the provisional nomenclature of Hofmann, they would come under the designation of nitrile bases; and in the decompositions in which morphia and codeine have been seen to be transformed, they would have had attached to them the elements of iodide of ethyl, for instance, as expressed thus:

$$C_{34}H_{19}NO_6 + C_4H_5I = C_{38}H_{24}NO_6, I \quad \text{and}$$
$$C_{36}H_{21}NO_6 + C_4H_5I = C_{40}H_{26}NO_6, I$$

the new salts becoming rather analogous to iodide of ammonium than to hydriodates of natural alkaloids.

Experiments made in the same direction, with others of the vegetable bases, would doubtless prove of considerable interest; since, notwithstanding both those to which I have given my attention appear to belong to the same class, as was perhaps to be expected from their being so closely allied in origin, it is extremely probable that alkaloids, contained in plants of a different natural family, will be found to possess different constitutions; I hope to examine a few.

I would venture to make one other remark before concluding this paper. The fact, that by the action of iodide of methyl upon morphia, a salt is produced, only isomeric and in no way identical with hydriodate of codeine, the base of the new salt differing so widely in character from the latter alkaloid, does not appear to me to afford great stimulus to any hopes of forming the natural alkaloids by this means; since, if we fail in the case of two natural products of the very same plant, it seems far less probable to bring about such a result as the production of a base identical with a natural formation, from a substance with which it has no relation, beyond a certain difference in their relative proportions of carbon and hydrogen.

In conclusion, I append a list of the salts I have examined, considered as iodides, in their dry and crystallized states:

Iodide of methylomorphia,	dried at 212°	$C_{36}H_{22}NO_6$, I
„ „ „	crystallized	$C_{36}H_{22}NO_6$, I + 2 HO
„ „ ethylomorphia,	dried at 212°	$C_{38}H_{24}NO_6$, I
„ „ „	crystallized	$C_{38}H_{24}NO_6$, I + HO
„ „ ethylocodeine is	anhydrous	$C_{40}H_{26}NO_6$, I
Platinum-salt of „	dried at 212°	$C_{40}H_{26}NO_6$, Cl, $PtCl_2$ + HO.